

CLAIMS

1. A nanocrystal oxide—glass mesoporous composite powder or thin film having a three-dimensional structure with regularly arranged mesopores.
2. A nanocrystal oxide—glass mesoporous composite powder or thin film having a hexagonal or cubic three-dimensional structure.
3. The nanocrystal oxide—glass mesoporous composite powder or thin film according to claim 1 or claim 2, wherein a porous structure framework contains uniform nanocrystal oxides.
4. The nanocrystal oxide—glass mesoporous composite powder or thin film according to any one of claims 1 to 3 having a large specific surface area in the range of 50 to 400m²/g.
5. A manufacturing method of nanocrystal oxide — glass mesoporous composite powder or thin film, comprising the steps of: using a block macromolecule or interface activating agent as a template, and adding hydrochloric acid (HCl) to a metal alkoxide or metal chloride, or an aqueous solution of PO(OC₂H₅)₃ or Si(OC₂H₅)₄(TEOS) or a solution obtained by dissolving these in alcohol such as ethanol; manufacturing powder having a glass phase metal oxide—inorganic oxide composite mesostructure with a sol-gel process; maturing and gelling this between room temperature and 90°C; removing the block macromolecule or interface activating agent by performing heat treatment thereto in the atmosphere at 350 to 400°C and manufacturing a glass phase metal oxide—glass phase mesoporous composite powder; and additionally performing heat treatment thereto at 400 to 700°C so as to change the phase of the glass phase metal oxide into crystallite.

6. A manufacturing method of nanocrystal oxide — glass mesoporous composite thin film, comprising the steps of: using a block macromolecule or interface activating agent as a template, adding hydrochloric acid (HCl) to a metal alkoxide or metal chloride, or an aqueous solution of $\text{PO}(\text{OC}_2\text{H}_5)_3$ or $\text{Si}(\text{OC}_2\text{H}_5)_4$ (TEOS) or a solution obtained by dissolving these in alcohol such as ethanol, and obtaining a sol solution by performing hydrolysis while adjusting the pH; forming a thin film having a glass phase metal oxide—inorganic oxide — block macromolecule (or interface activating agent) composite mesostructure on a substrate by delivering the sol solution in drops onto a substrate, rapidly rotating the substrate, and evaporating and gelling the solvent; maturing and gelling this between room temperature and 90°C ; removing the block macromolecule or interface activating agent by performing heat treatment thereto in the atmosphere at 350 to 400°C and manufacturing a glass phase metal oxide—glass phase mesoporous composite thin film; and additionally performing heat treatment thereto at 400 to 700°C so as to change the phase of the glass phase metal oxide into crystallite.
7. The manufacturing method of nanocrystal oxide — glass mesoporous composite powder or thin film according to claim 5 or claim 6, wherein an inorganic oxide of a stable glass phase is SiO_2 , P_2O_5 and B_2O_3 .
8. The manufacturing method of mesoporous powder or thin film according to any one of claims 5 to 7, wherein a dissimilar metal oxide such as MnO_2 , NiO , Fe_2O_3 , CuO , Li_2O , WO_3 , SnO_2 is added in a slight amount at the synthesizing stage, and the mesoporous powder or thin film is formed from a nanocrystal oxide—a glass

phase of inorganic oxide—dissimilar metal oxide ($-\text{MnO}_2$, $-\text{NiO}$, $-\text{Fe}_2\text{O}_3$, $-\text{CuO}$, $-\text{Li}_2\text{O}$, $-\text{WO}_3$, $-\text{SnO}_2$ or the like) having a multicomponent glass phase.

9. The manufacturing method of a nanocrystal oxide—a glass mesoporous composite powder or thin film according to any one of claims 5 to 8, wherein metal alkoxide or metal chloride is $\text{Ti}(\text{OC}_3\text{H}_7)_4$, $\text{Zr}(\text{OC}_4\text{H}_9)_4$, NbCl_5 , LiCl , NiCl_2 , FeCl_3 , CuCl_2 , MnCl_2 , SnCl_4 or WCl_5 .

10. A lithium battery, lithium intercalation electric device, photocatalytic device, solar battery or energy storage device using the nanocrystal oxide—glass mesoporous composite powder or thin film manufactured according to any one of claims 5 to 9.

11. A secondary battery configured with a nanocrystal oxide—glass mesoporous composite electrode having a three-dimensional structure with regularly arranged mesopores.

12. The secondary battery according to claim 11, wherein the average diameter of pores is 2nm to 10nm.

13. The secondary battery according to claim 11 or claim 12, wherein a framework of nanocrystal oxide—glass mesoporous composite having a hexagonal or cubic structure contains uniform crystallite oxides of several nano-orders.

14. The secondary battery according to any one of claims 11 to 13, wherein the thickness of a wall of the framework is 2 to 9nm.

15. The secondary battery according to any one of claims 11 to 14, wherein the nanocrystal oxide is one or more types of metal oxides selected from TiO_2 , NiO , MnO_2 , FeO , Fe_2O_3 , Fe_3O_4 , CoO , CoO_2 , CrO_2 , Co_3O_4 , WO_3 , SnO and SnO_2 .

16. The secondary battery according to any one of claims 11 to 15, wherein the glass phase is one or more types of inorganic oxides

selected from P_2O_5 , SiO_2 and B_2O_3 .

17. The secondary battery according to any one of claims 11 to 16, wherein the glass phase is a multicomponent glass phase containing one or more types of dissimilar metal oxides selected from MnO_2 ,
5 NiO , Fe_2O_3 , CuO , Li_2O , WO_3 , and SnO_2 at a molar ratio of 2% to 60% in relation to the glass phase.

18. The secondary battery according to any one of claims 11 to 16, wherein both an ionic conductive path and electronic conductive path are provided in the framework by adding ion conductive or
10 electron conductive dissimilar metal oxides in a network-shaped glass phase at a molar ratio of 2% to 60% in relation to the glass phase.

19. The secondary battery according to any one of claims 11 to 18, wherein the nanocrystal oxide—glass mesoporous composite is used
15 as the electrode of the secondary battery, and the energy density of charging (or discharging) is able to maintain a rate of more than 60% to 70% of 0.1A/g even when increasing the charging (or discharging) rate to ten times 0.1A/g (1.0A/g), and even one hundred times 0.1A/g (10A/g).

20. The secondary battery according to any one of claims 11 to 19, wherein the nanocrystal oxide—glass mesoporous composite is used as the electrode of the secondary battery so as to increase the surface area, and the charging/discharging capacity has a large capacity of 1.0 to 5.0 times the maximum theoretical capacity in
25 relation to active oxides.

21. The secondary battery according to any one of claims 11 to 20, wherein the nanocrystal oxide—glass mesoporous composite is used as the electrode of the secondary battery, and a high reversible ratio

of 95% or higher is realized even when increasing the charging (or discharging) rate to ten times 0.1A/g (1.0A/g), and even one hundred times 0.1A/g (10A/g).

22. The secondary battery according to any one of claims 11 to 21,
5 wherein the nanocrystal oxide—glass mesoporous composite is used as the electrode of lithium, and a high reversible capacity of 60% to 70% or higher of the initial capacity is realized after a charging/discharging cycle of several hundred cycle even when increasing the charging (or discharging) rate to ten times 0.1A/g
10 (1.0A/g), and even one hundred times 0.1A/g (10A/g).

23. The secondary battery according to any one of claims 11 to 21, wherein a nanocrystal oxide—a glass phase of inorganic oxide—dissimilar metal oxide to which a slight amount of dissimilar metal oxide was added has a high reversible capacity at a rate of 40% to
15 70% or higher of 0.1A/g even when the charging/discharging rate is increased to a rate of one hundred times, five hundred times or one thousand times 0.1A/g.

24. The secondary battery according to any one of claims 11 to 23 having a high reversible ratio ($r > 95\%$).

20 25. A lithium storage device such as a capacitor or super capacitor according to any one of claims 11 to 24 utilizing oxidization/reduction of lithium ion.